The Crystal and Molecular Structures of Bis(ethylenedithio)-tetrathiafulvalene

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Synopsis. The X-ray crystal structure analysis of a sulfur containing π-donor molecule, bis(ethylenedithio)-tetrathiafulvalene, (BEDT-TTF) shows that the BEDT-TTF molecule is nonplanar and that the crystal is composed of pairs of BEDT-TTF.

Recent discoveries of the superconductivities of the organic conductors based on a sulfur containing π-donor molecule, bis(ethylenedithio)tetrathiafulvalene (abbreviated as BEDT-TTF hereafter) have aroused a considerable interest.[1] The crystals of BEDT-TTF compounds show a characteristic two-dimensional (abbreviated as 2-D hereafter) array of BEDT-TTF,[2] whereas the molecular metals so far reported have 1-D stacks of planar π-donor and/or acceptor molecules. The examination of the intermolecular overlap integrals of HOMO, from which the conduction bands are formed, indicates 2-D properties of BEDT-TTF compounds.[2-4] Moreover, β-(BEDT-TTF)$_2$PF$_6$ has an open Fermi surface perpendicular to the direction approximately parallel to the averaged molecular plane of BEDT-TTF, which shows definitely an important role of the 2-D intermolecular interactions in the organic conductors.[5,6]

In this paper, we will report the crystal structure of the neutral BEDT-TTF molecule.

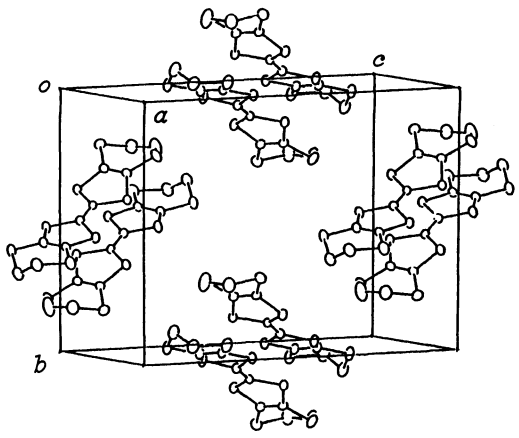

Fig. 1. The crystal structure of BEDT-TTF.

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Results and Discussion

Crystal Data: $C_{10}H_8S_8$, M=384.7, monoclinic, space group, $P2_1/c$, a=6.614(11), b=13.985(2), c=16.646(3) Å, β=109.55(2)°, U=1449.6 Å^3, Z=4, D_x=1.76 g cm^{-3}, μ(Mo $K\alpha$)=11.6 cm^{-1}. Intensities were measured by the θ—2θ scan technique on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation (2θ<55°) and were corrected for usual Lorentz and polarization effects, but not for the absorption. The maximum dimension of the crystal used was 0.3 mm. The structure was solved by the direct method and refined by the least-squares procedure (currently R=0.052), using 2262 reflections ($|F_o|>3\sigma(|F_o|)$). The hydrogen atoms were refined isotropically, but the temperature factors of two of them became very large (10 Å^2 and 8 Å^2), which is probably due to the large thermal motion of the ethylene groups. Therefore, the hydrogen atoms were omitted in the final refinement. The atomic coordinates are given in Table 1.[7] The crystal structure is shown in Fig. 1.

The crystal is composed of the pairs of BEDT-TTF molecules. Similar paired structure of BEDT-TTF has also been found in the crystals of BEDT-TTF monocation salts ((BEDT-TTF)X(THF); X=ClO_4 or ReO_4).[8] The bond lengths and angles are shown in

Table 1. Atomic Parameters of BEDT-TTF

	x	y	z	B_{eq}/Å^2
S(1)	0.2564(2)	0.3834(1)	0.0163(1)	3.6
S(2)	0.6211(2)	0.3592(1)	−0.0457(1)	4.0
S(3)	0.0050(2)	0.5067(1)	−0.1531(1)	3.7
S(4)	0.3704(2)	0.4826(1)	−0.2142(1)	2.6
S(5)	0.4054(2)	0.2299(1)	0.1475(1)	5.4
S(6)	0.8167(2)	0.2029(1)	0.0790(1)	3.8
S(7)	−0.2917(2)	0.5081(1)	−0.3143(1)	5.9
S(8)	0.1430(2)	0.5522(1)	−0.3884(1)	3.2
C(1)	0.3599(7)	0.4049(3)	−0.0667(3)	2.8
C(2)	0.2581(7)	0.4554(4)	−0.1353(3)	2.8
C(3)	0.4421(7)	0.2937(4)	0.0634(3)	3.3
C(4)	0.6073(8)	0.2816(4)	0.0353(3)	2.8
C(5)	−0.0354(7)	0.5356(4)	−0.2599(3)	3.3
C(6)	0.1290(7)	0.5240(4)	−0.2879(4)	2.7
C(7)	0.6767(11)	0.2173(7)	0.2197(4)	5.9
C(8)	0.8566(10)	0.2210(6)	+0.1904(4)	4.9
C(9)	−0.2893(9)	0.5803(5)	−0.4221(4)	5.8
C(10)	−0.0933(10)	0.6255(5)	−0.4309(3)	6.9

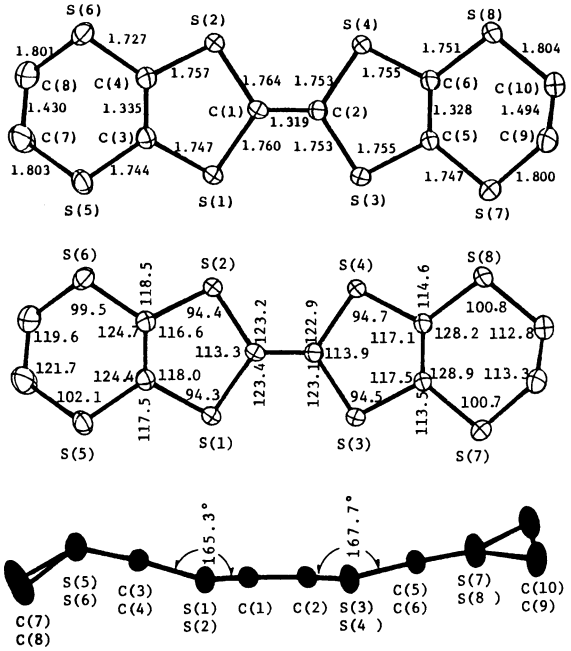

Fig. 2. Molecular structure of BEDT–TTF. Estimated standard deviations of bond lengths are 0.007—0.012 Å and those of bond angles are 0.6—1.0°.

Fig. 2. The mean bond length of C–S in the TTF skeleton is 1.751 Å and that of C=C is 1.327 Å. The structure analyses of several BEDT-TTF salts show that the C=C bonds become longer and the C–S bonds become shorter with the increasing formal charge(ρ) of BEDT-TTF$^{+\rho}$ molecule: r(C=C)=1.33 Å(ρ=0), 1.35(ρ=0.5), 1.38(ρ=1); r(C–S)=1.751(ρ=0), 1.745(ρ=0.5), 1.724(ρ=1). This is due to the symmetry of HOMO of BEDT-TTF which has nodal planes on the every C–S bond.

The BEDT-TTF molecule is nonplanar. The molecule is composed of three planes of tetrathio-substituted ethylene moieties (Fig. 2). The mode of overlapping of the paired molecules is shown in Fig. 3a. Despite of the pair structure of BEDT-TTFs, the shortest S···S distance (3.69 Å) is almost equal to the van der Waals distance (3.70 Å). Closer intermolecular contacts are found along the a axis (Fig. 3b). The sulfur atoms play a central role for the formation of the characteristic transverse intermolecular contacts. As described before, the side-by-side arrangement of BEDT-TTF is a common structural feature of the conducting BEDT-TTF salts. It is of interest that similar arrangement is also found even in the insulating neutral BEDT-TTF crystal.

Calculations were carried out partly on PANAFACOM U1300 computer of Toho University and mainly on HITAC M-200H computer at the Computer Center of The University of Tokyo, using the local version of the UNICS.[9]

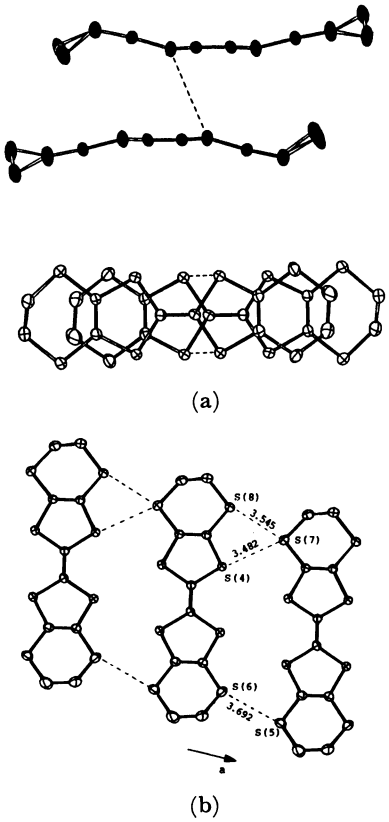

Fig. 3. (a) The mode of overlapping of the paired BEDT-TTFs. The dotted line indicates the short S···S contact (3.69 Å). (b) Molecular arrangement along the a axis.

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